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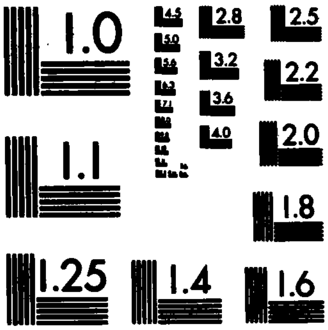

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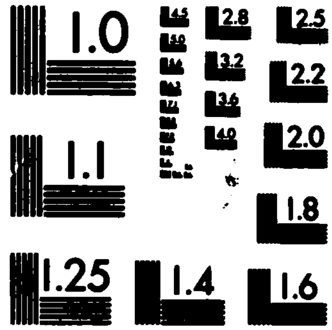

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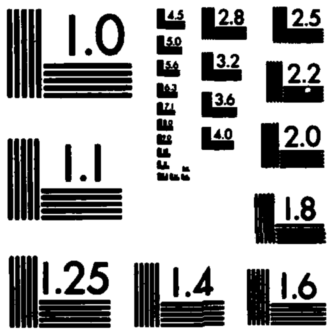

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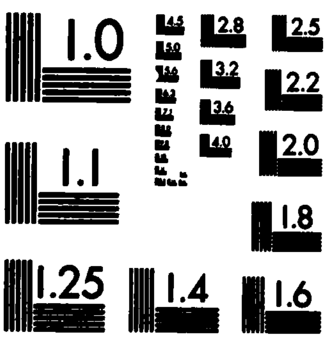

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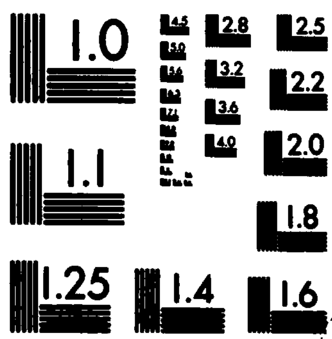

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TECHNICAL REPORT NO. 6

PHOTOELECTROCHEMICAL DEPOSITION OF METALS ONTO p-SILICON USING AN INTERNAL CELL

by

T. L. Rose, D. H. Longendorfer and R. D. Rauh

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EIC Laboratories, Inc.
111 Chapel Street
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Spatially defined photoelectrochemical deposition of low work function metals onto p-Si has been observed, operating through the local cell

$$M^{+n} + ne^- \xrightarrow[p\text{-}Si]{h\nu} M^o$$

$$\xleftarrow[dark]{}$$

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PHOTOELECTROCHEMICAL DEPOSITION OF METALS ONTO p-SILICON USING AN INTERNAL CELL

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ABSTRACT

Spatially defined photoelectrochemical deposition of low work function metals onto p-Si has been observed, operating through the local cell

$$M^{+n} + ne^- \xrightarrow[p\text{-}Si]{h\nu} M^o$$

$$\xleftarrow[dark]{}$$

Some M^o must be incorporated initially onto the Si surface via a low resistance contact. With M = Zn or Cd, a large band bending is induced at the semiconductor/plating electrolyte junction, resulting in highly efficient imaging. For the more noble metals, Cu and Ni, the bending is very small or nonexistent, and this kind of imaging is not observed.

There has been considerable recent interest in light-localized imaging processes on semiconductor surfaces for producing metal contacts and etched or oxide patterns. In the case of metal deposition, patterns have been generated electrolytically by light-induced, localized heating which decreases plating overpotential[1], or photolytically by localized photoreduction of the metal precursor.[2,3] Metal electrodeposition activated by charge carriers produced in the semiconductor has also been achieved, with charge separation of light generated electron-hole pairs occurring as a result of the semiconductor-electrolyte junction (photoelectrochemical deposition).[4] We recently reported photoelectrochemical deposition of microscopic resolution patterns of several metals onto p-GaAs and p-Si electrodes under external potential or current control in an electrochemical cell with standard plating baths and electrolytes.[5] In principle, these purely electronic deposition processes can be extremely efficient, with an upper limit of one atom-equivalent deposited for each photon absorbed. For example, a He-Ne laser spot of only 10 mW/cm^2 intensity projected onto a p-Si electrode in an electrolyte with monovalent metal ions having an equivalent weight of 100 and a density of $10g/cm^3$ can induce an initial plating rate of about $100Å/cm^2$ sec.

In this communication we consider the possibility of photoelectrochemical deposition of metal patterns on semiconductors without the aid of an external power supply, i.e., an <u>electroless</u> process. Here, we require that complementary reduction and oxidation occur in illuminated and dark regions, respectively. For redox couples which induce large band bending and, hence, affect efficient charge separation, reactions would involve predominantly minority carriers in the lighted areas and majority

Table 1 compares the current density developed in the Cu, Ni, Cd and Zn cells on illumination with 1.2 mW/cm^2 tungsten-halogen light. With Cd and Zn, where the photoelectrodeposition is very efficient, a deposit is almost instantly visible when the shorted photoelectrode is illuminated. Negligible plating or photocurrent was observed for Ni or Cu. Therefore, the deposition quantum efficiency was highest for the more negative lying metal couples. This result is understandable on the basis of the band bending in the p-Si electrode, shown in Figure 2 for the Zn and Cu cells. The very negative internal bias exerted by Zn, for example, creates a large band bending at the semiconductor-electrolyte interface. On the other hand, the $Cu^{+2/0}$ potential is near the flat band potential of p-Si[6], and little band bending (and hence separation of light generated electrons and holes) can be expected.

The current-voltage curves of p-Si in the Zn and Cu plating baths reveal the details of the electrode reactions and are shown in Figure 1b. In the Cu^{+2} electrolyte, the Cu is plated and stripped on Si near its reversible potential (measured independently). The plating onset potential is relatively unaffected by illumination. Enhanced plating current with illumination is only observed when the electrode is externally back-biased. This current-voltage behavior is typical of electrochemical reactions which occur at potentials positive of the flat band voltage in p-type photoelectrodes, all charge exchange in the dark probably occurring via the valence band. Since the Cu plating and stripping reactions on p-Si are near to the measured reversible potential, the deposit appears to be electrically ohmic.

In the Zn^{+2} electrolyte at the same pH, several new features are observed. First, a cathodic process is seen in the light, starting at ∿-0.3V vs. SCE. On holding the electrode at this voltage, Zn deposits on the illuminated electrode surface. The deposition reaction is most likely mixed with some hydrogen evolution or Si-H formation, since a small background cathodic photocurrent is observed in the absence of Zn^{+2}. The Zn photodeposit is stripped at potentials positive of -0.6V, indicated by a broad anodic peak. Some reversible plating and stripping of Zn at its thermodynamic potential of ∿-1V vs. SCE is often seen in the dark, as indicated in Figure 1b. This process, which varies in magnitude for different samples, is unaffected by light and probably reflects leakage of electrolyte into the contact region or "decoration" of electrically degenerate electrode defects. The separation of this stripping peak from that of the photoplate signifies the rectifying nature of the latter. We see that metals that tend to plate with high photoelectrochemical efficiency in this type of cell are also those with a large work function difference from that of the semiconductor. Thus, the photoplate is likely to be rectifying and will continue to grow as long as light can get through to the junction.

A demonstration of the "electroless" photoelectrochemical deposition of a metal image, in this case of a scanned laser spot (50 μm, $1/e^2$ diam.), onto a p-Si wafer is shown in Figure 3. The back, nonilluminated side of the substrate is plated with the metal prior to imaging, preferably over an ohmic contact to minimize the stripping overpotential. The front surface of the wafer is then exposed to the projected light beam, and

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TABLE I. SHORT CIRCUIT PHOTOCURRENTS IN TWO ELECTRODE PHOTOELECTROCHEMICAL CELLS OF THE CONFIGURATION: METAL|M^{+2} ELECTROLYTE|p-Si|OHMIC CONTACT.[a]

Electrolyte (pH 3.1)	$V(M^{+2/0})$, Volts. vs. SCE (Measured)	Initial Photocurrent[b] ($\mu A/cm^2$)
No added metal ion	~0.3 (Pt)	<0.5
0.5M $NiSO_4$	0.250	<0.5
0.5M $CuSO_4$	0.070	10
0.5M $CdSO_4$	-0.67	180
0.5M $ZnSO_4$	-1.022	500

[a] Measurements are made under 1.2 mW/cm^2 illumination from a tungsten-halogen source.

[b] Photocurrent decreases as thickness of deposit increases.

FIGURE CAPTIONS

Fig. 1 Current-voltage curves for p-Si photocathode. (a) Hypothetical curves showing overlap region (shaded) between the anodic, dark current and cathodic photocurrent necessary for "electroless" imaging; (b) cyclic voltammograms for p-Si in Zn plating electrolyte and in Cu plating electrolyte with 0.5M MSO_4 and pH = 3.1. Scan rate for (b) is 100 mV/sec. Broken line, dark; solid line, 1.2 mW/cm^2 tungsten-halogen light illumination.

Fig. 2 Band diagrams for p-Si ohmically contacted with Cu (a) and Zn (b) and immersed in their respective plating electrolytes: cb = conduction band, vb = valence band, fl = Fermi level. Voltages of the metal couples are those measured in plating baths in Fig. 1.

Fig. 3 Metal deposit produced by scanning a 50 μm He-Ne laser spot across a p-Si substrate immersed in a 0.1M $ZnSO_4$ electrolyte. A layer of Zn had been plated onto the back side of the Si. Following Zn deposition, the crystal was dipped into an electroless Au plating solution to enhance the contrast of the plated regions.

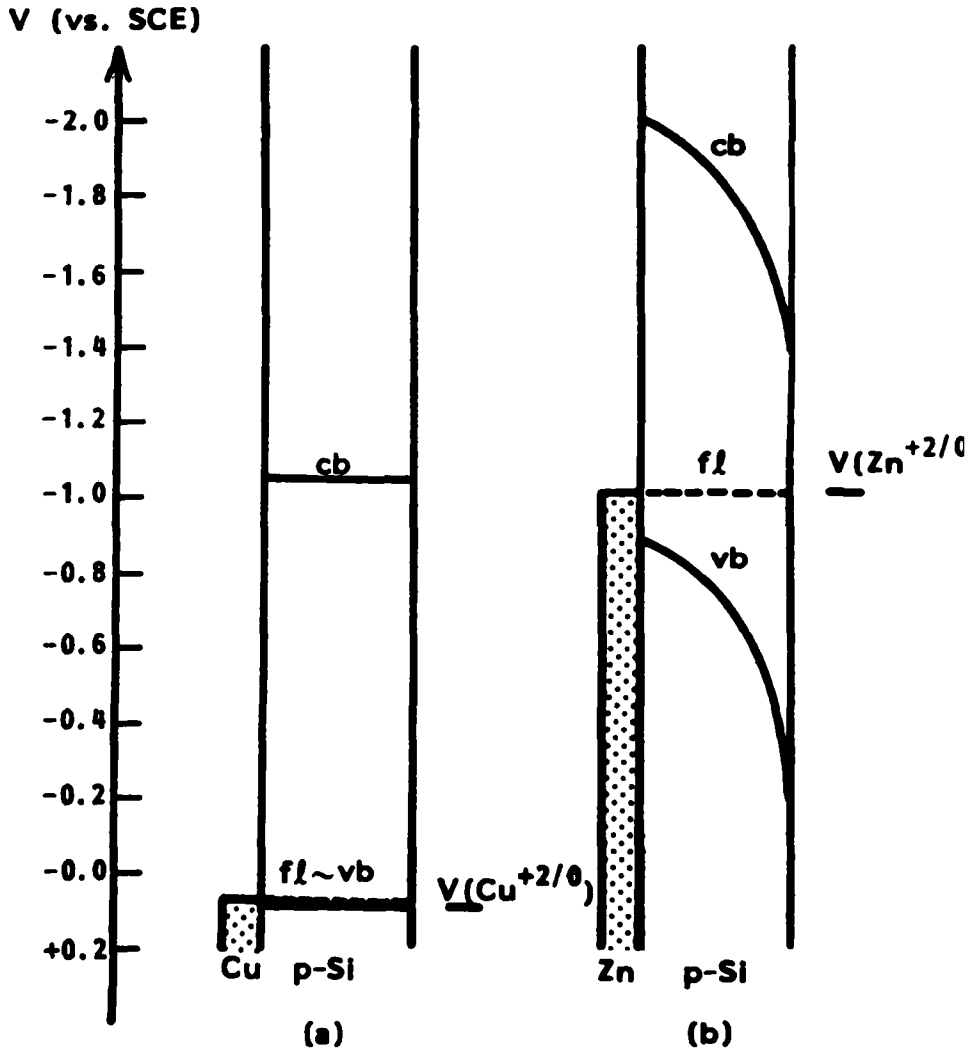
V (vs. SCE)
-2.0
-1.8
-1.6
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
-0.0
+0.2
cb
fℓ~vb
V(Cu+2/0)
Cu
p-Si
(a)
cb
fℓ
V(Zn+2/0
vb
Zn
p-Si
(b)

FIGURE 2

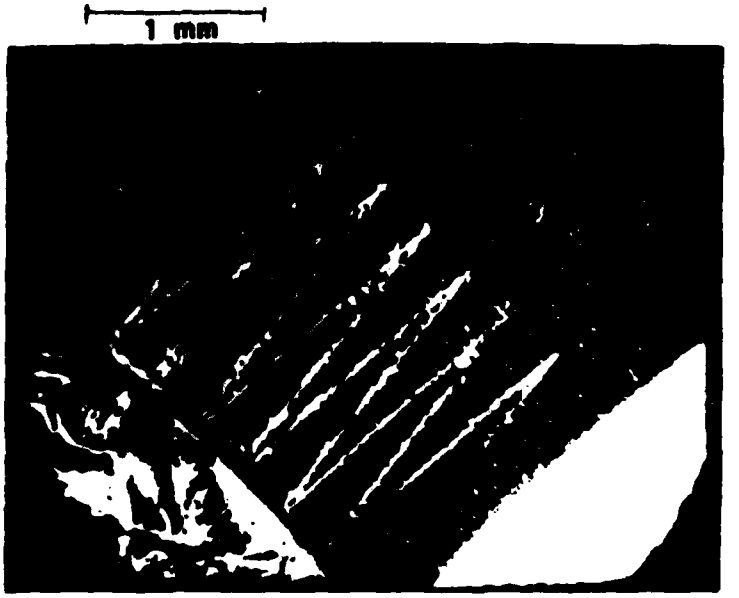

FIGURE 3

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